High Energy Electron Diffraction Reveals Bonding in Metals and Alloys

A.G. Fox
Center for Materials Science and Engineering, Naval Postgraduate School, Monterey, CA93940

Many important properties of engineering materials depend on the spatial distribution of the electrons responsible for atomic bonding. The electron charge distribution can be obtained from low angle structure factors. This work has made extensive use of the Berkeley 1.5MeV HVEM to measure the low-angle structure factors and temperature factors of simple metals and alloys with unprecedented accuracy (better than 0.1%) by employing the critical voltage technique. In conjunction with theoretical calculations, this has uncovered the bond distribution in many elements and binary alloys of interest in materials science.

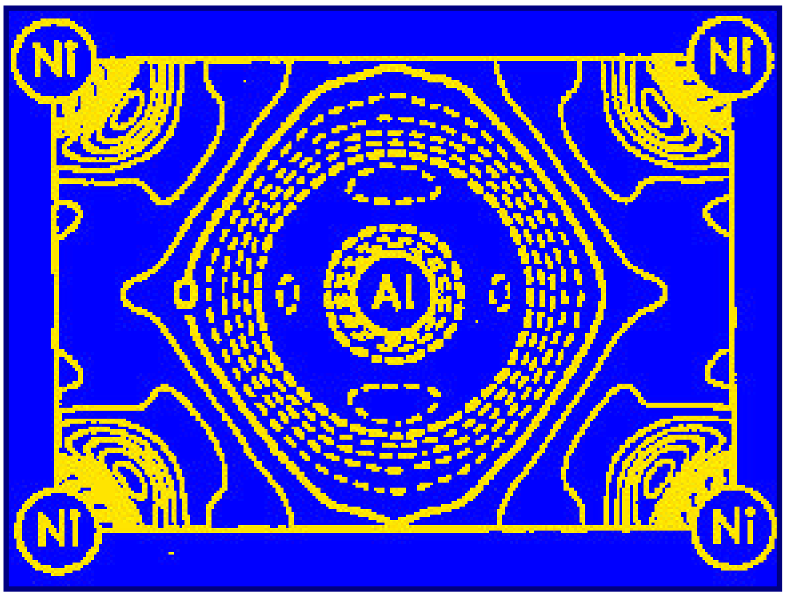
Background – The distribution of electron charge density represents the type and strength of bonding in a material and can be determined by measuring the low angle structure factors. Typically, x-ray and neutron diffraction are used for these measurements, but electrons, because of their stronger interaction with solids, are a more sensitive probe of the low-angle structure factors. However, inelastic scattering in the electron diffraction patterns makes it difficult to obtain accurate intensity data. The critical voltage effect circumvents this limitation by monitoring dynamical degeneracies in electron diffraction patterns as a function of temperature and electron energy. For many engineering materials, critical voltages are in the range of several hundred keV to above 1MeV and thus require a high voltage electron microscope for analysis.

Accomplishment – This work established the bond distribution in such metals as Be, Al, Si, Cr, Fe, Ni, Cu, Zn, solid solutions such as AlLi, FeCr and CuAu, and the intermediate phases TiAl, NiAl and CoAl [1-16]. For all these materials, the bonding was comprised of both metallic and covalent components, and the directionality of the covalent bonding was consistent with elastic and magnetic anisotropies. In the primary solid solutions charge transfer effects between atoms were detected and, in the B2 intermediate phases NiAl and CoAl, ionic components of bonding were found.

Over the period from 1984 to 1993, NCEM users A. Fox, R. Fisher and S. Menon used the Berkeley 1.5 MeV high voltage electron microscope at NCEM to measure low-angle structure factors via the critical voltage technique. This technique involves setting a second or higher order reflection in a systematic row to the exact Bragg reflecting condition and then measuring the voltage at which this reflection passes through a minimum. These experiments allow measurement of low-angle structure factors and Debye-Waller factors with better than 0.1% accuracy. The team measured low-angle structure factors of the pure metals Be, Al, Si, Cr, Fe, Ni, Cu, Zn as well as the primary solid solution alloys AlLi, FeCr and CuAu. In addition, measurements were also made on the intermetallic alloys γ-TiAl, β-NiAl and β-CoAl.

As a result of these measurements and theoretical calculations, information about the electron charge density distributions of these metals and alloys has been generated. For example, the figure shows a (110) section of the deformation electron density distribution (DEDD) for β-NiAl. This is essentially a plot of the charge difference distribution between a free atom representation of β-NiAl and that of β-NiAl in the solid state. This DEDD shows that bonding in β-NiAl is a combination of ionic, covalent and metallic types with electrons depleted from aluminum atom sites and with build-up of charge at nickel atom sites. In addition, there is build-up of electron charge between nearest-neighbor atoms in <111> directions (near Ni atom sites) typical of covalent-like bonding.

Since 1993, the development of energy filters has made it possible to obtain accurate measurements of convergent beam electron diffraction intensities at intermediate voltages using a new generation of electron microscopes. Low-angle structure factors of Si, Cu and Ni obtained from energy-filtered diffraction are in excellent agreement with the results previously obtained by the critical voltage technique. This work shows that it is possible to perform quantitative transmission electron diffraction in the TEM so that a complete crystallographic and chemical analysis of almost any unknown crystalline sample can be made with a spatial resolution of about 1 nm.



(110) Deformation electron density distribution for β -NiAl (simple cubic with a = 0.2887 nm). The contour spacing is 10 enm^{-3} with dashed contours indicating electron depletion (from reference 16).

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